

PRELIMINARY

N65-88669

FACILITY FORM 602

N65-88669
(ACCESSION NUMBER)

18
(PAGES)

TMX-57477
(NASA CR OR TMX OR AD NUMBER)

(THRU)

(CODE)

(CATEGORY)

PRELIMINARY RESULTS OF DIFFUSION STUDIES
OF COMMERCIALLY AVAILABLE COATINGS ON
Mo-0.5 Ti MOLYBDENUM ALLOY SHEET
AT 2500° F

By

Bland A. Stein and W. Barry Lisagor
Langley Research Center, NASA

Prepared for the Seventh Meeting of
The Refractory Composites Working Group

March 12, 13, 14, 1963

Sunnyvale, Calif.

PRELIMINARY

PRELIMINARY

PRELIMINARY RESULTS OF DIFFUSION STUDIES OF COMMERCIALY AVAILABLE COATINGS ON Mo-0.5 Ti. MOLYBDENUM ALLOY SHEET

INTRODUCTION

Proposed applications of refractory metals in the thermal protection systems of aerospace vehicles may involve repeated flights with temperature histories from 2000° F to 3000° F for 15 minutes or longer during each flight. The high densities of the refractory metals makes it mandatory to utilize them in very thin gages. For applications of this type, the detrimental effects of diffusion must be considered. The refractory metal substrate must retain sufficient strength and ductility over the intended range of usefulness. The coating must not embrittle the refractory metal substrate during its application or in subsequent service. It must provide a barrier to embrittling atmospheric gases at high temperatures. Furthermore, solid state diffusion between coating and substrate must be limited because any decrease in substrate thickness will result in a corresponding loss of strength in the structural component.

Preliminary results of a NASA study to determine the oxidation protection afforded by several commercially available silicide base coatings to Mo-0.5 Ti molybdenum alloy sheet were presented at the Sixth Meeting of the Refractory Composites Working Group, reference 1. The complete results of this oxidation study will be presented as a NASA Technical Note in the near future. Utilizing specimens obtained from the same lot as those reported in reference 1, the present study was undertaken:

- (1) To determine whether the coatings had embrittled the Mo-0.5 Ti sheet beyond the range of usefulness in the coating application.

PRELIMINARY



PRELIMINARY

- 2 -

(2) To determine the magnitude of substrate loss due to solid-state diffusion during various exposures in air at 2500° F.

(3) To obtain some insight into the mechanisms involved in the oxidation protection and solid-state diffusion processes by identification of the several phases present in the silicide based coatings after 2500° F exposure in air.

SPECIMENS, EQUIPMENT, AND PROCEDURES

The specimens used in this investigation were small Mo-0.5 Ti coupons, 1-5/8 inch by 3/4 inch by 0.012 inch (nominal before coating). The coated specimens were supplied to NASA during the period from July to December 1961. The coatings investigated are listed in table I.

The specimens were heated at ambient pressure in slowly moving air at 2500° F in an electric furnace and continuously weighed. For each coating one specimen was sectioned as coated, another after 1 hour continuous exposure, another after 8 hours continuous exposure, and another after coating failure as evidenced by 10 percent weight loss in the specimens due to the formation of volatile MoO_3 . For these failed specimens, enough unoxidized areas remained to permit satisfactory thickness determinations.

Specimens were sheared warm, embedded on edge in Lucite, ground in a conventional manner, and polished on a vibratory polisher using etch-polish-etch procedures with MuraKami's etch. Thickness measurements were made on a bench microscope at 150X magnification using a filar micrometer eyepiece

PRELIMINARY

PRELIMINARY

- 3 -

calibrated against a ruled grating. Each measurement reported represents an average of at least 12 readings on each specimen. Microhardness measurements utilizing the Knoop indenter with a 100 gram load were made in 2 cross sectional traverses and several indentations were made on the centerline of the substrate. Indentations were also made in each of the various layers of the coating where possible.

Coating phase identifications were made by combining metallographic examinations and x-ray diffraction analyses. The procedure consisted of obtaining diffraction records by exposing the face of the specimen to Cu K α radiation, grinding off 0.0002 to 0.0005 inch and obtaining another pattern until the Mo-0.5 Ti substrate was reached. Comparisons between analyzed x-ray records and photomicrographs of the same specimen on edge made possible identification of the coating phases present, with microhardness verifications in some cases.

RESULTS AND DISCUSSION

Metallography and Microhardness

The first two figures will review some of the results presented in reference 1. Figure 1 presents the oxidation test results under constant and cyclic temperature exposure. In general the life of the coated specimens was greatly decreased under cyclic temperature exposure. In figure 2, a summary of the tensile test results of reference 1 is presented.

For briefness in this preliminary report, photomicrographs, thickness

PRELIMINARY

PRELIMINARY

- 4 -

determinations and hardness data will be presented for 1 coating only. Similar data are available for the other coatings investigated and will be presented in a forthcoming NASA Technical Note.

The AMF Kote 2 is applied by a 2 cycle pack cementation process. Half of the specimens supplied to NASA were subjected to a "preglassing" treatment consisting of an exposure for 1 hour at 2800° F in air. Figure 3 presents photomicrographs of typical areas and average hardness values for preglassed AMF coated specimens. The coating and preglassing procedures completely recrystallized the Mo-0.5 Ti substrate. The as coated, preglassed, specimens which had a room temperature tensile strength of 60 ksi and an elongation of 3 percent (figure 2), had a substrate Knoop hardness of 252. These properties are substantially the same as those obtained for uncoated Mo-0.5 Ti sheet exposed for 1 hour at 2800° F in vacuum, which indicates that any embrittlement due to coating or preglassing procedures was not a large effect.

Average thickness values are shown graphically in figure 4 along with substrate hardness and percent recrystallization as functions of process and exposure time at 2500° F. After full recrystallization the substrate hardness did not change substantially with 8 hours exposure time and showed only a small increase after 1000 hours exposure. The reduction in substrate thickness and increases in coating thickness and total specimen thickness with exposure time at 2500° F are shown in figure 4.

Comparison of Results for Various Coatings

The hardness traverses showed that for each coating the hardness of the substrate was uniform through the thickness or uniform for the recrystallized and unrecrystallized areas. These data indicate that the application of the

PRELIMINARY

PRELIMINARY

- 5 -

coatings investigated did not embrittle the substrate beyond its range of usefulness. This effect was confirmed by the tensile test results (figure 2). The substrate properties were significantly affected by the magnitude of the temperature and time utilized in the coating application and not by the presence of the coating. Hardness values for all specimens after the various 2500° F exposures in air were also uniform through the substrate thickness.

The magnitude of the decrease in substrate thickness with exposure time in air is indicated in figure 5 by the test points. An empirical relationship of the type

$$S = S_0 - At^B \quad (1)$$

where

S = substrate thickness at time t

S_0 = as-coated substrate thickness

t = exposure time at 2500° F in air

A = constant

B = constant

was found to describe the substrate thickness decrease with time with fair accuracy for the coatings investigated. The constants A and B for equation (1) are presented in table II. The curves in figure 5 were calculated from equation (1). Although the coatings investigated varied considerably in both process and additive elements other than silicon, the substrate thickness decreased at approximately the same rate for all coatings. This indicates that the diffusion problem encountered is basic in nature, involving the diffusion of silicon into molybdenum with only slight variations caused by the other

PRELIMINARY

PRELIMINARY

- 6 -

elements present. The magnitude of substrate thickness decrease for these silicide base coatings on Mo-0.5 Ti sheet was on the order of 0.001 to 0.003 inch in the first 10 hours at 2500° F. This indicates that solid state diffusion barriers may be required when coated refractory metals of thin gage are utilized for high temperature service in aerospace vehicles.

Identification of Coating Phases

Two coatings were chosen for the x-ray investigations. The Boeing Disil is a pure silicide coating with no additives and thus provides a reference for the reactions which occur at high temperatures in silicide base coatings. The AMF Kote 2 was selected because of its long oxidation life at high temperatures as shown in figure 1. It is assumed that if the effects of the additions to the silicon in the AMF coating pack were understood, a possible explanation for the long 2500° F oxidation life could be postulated.

Boeing Disil. - In the as-coated condition, the Boeing Disil coating was essentially a single phase layer of MoSi_2 . Figures 6(a) and 6(b) show highly magnified views of a typical Disil coated specimen after 21.2 hours at 2500° F, with the various phases identified. The original MoSi_2 layer has become quite thin after diffusion occurred. The appreciable Mo_5Si_3 content in the outer layer indicates that this compound formed at the expense of the MoSi_2 with the liberated silicon participating in the formation of an outer glassy layer. It is this thin layer of SiO_2 , evident on inspection of specimens after high temperature tests, which has been postulated to provide oxidation protection and self healing characteristics. Adjacent to the $\text{MoSi}_2 + \text{Mo}_5\text{Si}_3$ is a relatively wide band of Mo_3Si , found to be preferentially oriented with growth occurring in the 100 direction perpendicular to the substrate.

PRELIMINARY

PRELIMINARY

- 7 -

The band adjacent to the Mo-0.5 Ti substrate was not identifiable by x-ray techniques but was identified by microhardness measurements as "Mo Si", normally found by siliconizing molybdenum. This band did not grow appreciably in size but apparently reacted to form Mo_3Si .

AMF Kote 2. - The photomicrographs in figure 3 show the growth and phase changes in the coating during exposure at 2500° F. Before preglassing the coating was essentially a single phase layer of MoSi_2 . Figure 7 shows a highly magnified view of an AMF Kote 2 preglassed specimen after 120 hours at 2500° F in air, with the phases identified. These phases are identical to those previously described for the Boeing Disil coating excepting for the existence of an additional phase, identified as $\text{Mo}_5(\text{B},\text{Si})_3$. This layer appears to provide no protection against oxidation or diffusion, but it does serve as an indication of the direction of mass flow. After extended length of time at 2500° F, this phase moves in a direction towards the outer glassy layer, indicating that diffusion of silicon inward is the predominating mass flow.

The evidence of a boron compound in the AMF Kote 2 coating indicates that boron might also be found in the outer glassy layer, producing borosilicate glass in addition to the silica produced by oxidation of the silicon. The glassy layer of the AMF Kote 2 specimens may therefore be expected to be a viscous liquid over a temperature range from below 2000° F to over 3000° F. The boron and traces of other additives, particularly aluminum, in the pack could also act to retard recrystallization of the outer glassy layer, thereby retaining oxidation protection and self healing characteristics in the AMF coating for long periods of time at high temperatures.

PRELIMINARY

PRELIMINARY

- 8 -

CONCLUDING REMARKS

From the preliminary results presented herein, the following may be concluded:

(1) Solid state diffusion barriers may be required when using silicide base coatings on thin gage refractory metals at high temperatures in aerospace vehicles.

(2) The addition of detectable amounts of boron in one of the coatings appears to have provided a significant increase in oxidation protection over the other silicide base coatings investigated for Mo-0.5 Ti molybdenum alloy sheet.

(3) The application of the coatings investigated did not embrittle the Mo-0.5 Ti sheet beyond the range of usefulness. All coatings investigated appear to have provided a diffusion barrier for the substrate against atmospheric gases at 2500° F until failure.

REFERENCES

1. Rummier, D. R., Stein, B. A., and Pride, R. A.: Preliminary Results of a Comparative Study of Several Commercially Available Oxidation Resistant Coatings on Mo-0.5 Ti alloy Sheet. Presented at the Sixth meeting of the Refractory Composites Working Group, June 1962, Dayton, Ohio.

PRELIMINARY

PRELIMINARY

- 9 -

TABLE I.- COATINGS INVESTIGATED ON Mo-0.5 Ti SHEET

COATING	METHOD OF APPLICATION	CONSTITUENT ELEMENTS
AMF KOTE 2	2-CYCLE PACK CEMENTATION	Si, B, Cr, Cb, Al, C
BOEING DISIL	FLUIDIZED BED	Si
CHANCE VOUGHT	2-CYCLE PACK CEMENTATION	Si, Cr, B, C, Al, Ti, Cb
CHROMALLOY W-2	2-CYCLE PACK CEMENTATION	Si, Cr
PFAUDLER PFR-5	2-CYCLE PACK CEMENTATION	Si, Cr
PFAUDLER PFR-6	1-CYCLE PACK CEMENTATION	Si, Cb

PRELIMINARY

PRELIMINARY

- 10 -

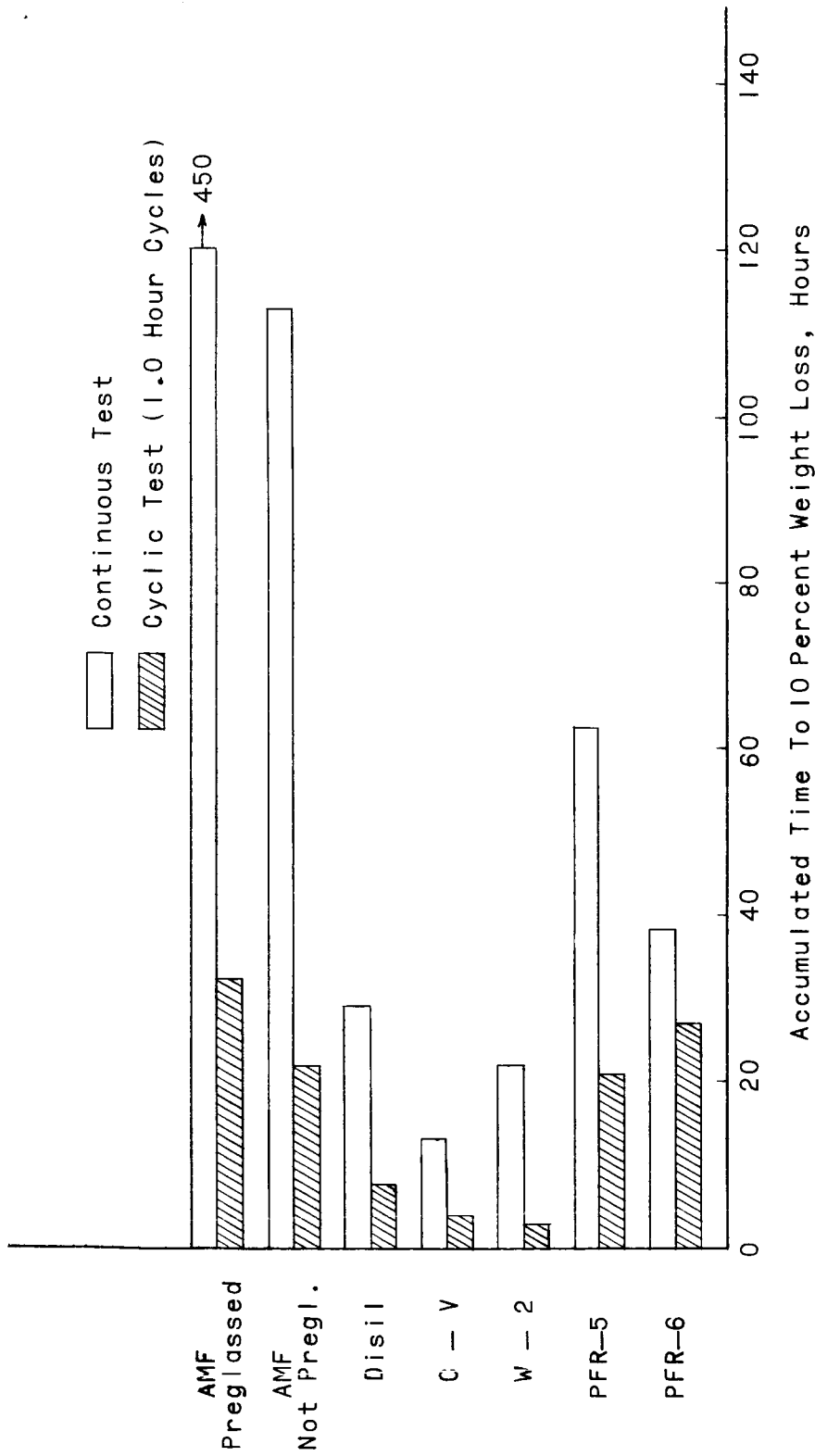
TABLE II.- CONSTANTS FOR THE FORMULA $S = S_0 - At^B$ DESCRIBING
THE Mo-0.5 Ti SUBSTRATE THICKNESS DECREASE WITH
EXPOSURE TIME IN AIR AT 2500° F

Coating	S_0 , Inches	A	B
AMF Kote 2 Not Preglassed	0.0099	0.00030	0.5000
AMF Kote 2 Preglassed	0.0092	0.00165	0.1153
Boing Disil	0.0081	0.00033	0.4510
Chance Vought	0.0106	0.00110	0.0762
Chromalloy W-2	0.0109	0.00073	0.5090
Pfandler PFR-5	0.0091	0.00207	0.1323
Pfandler PFR-6	0.0097	0.00171	0.1355

PRELIMINARY

PRELIMINARY

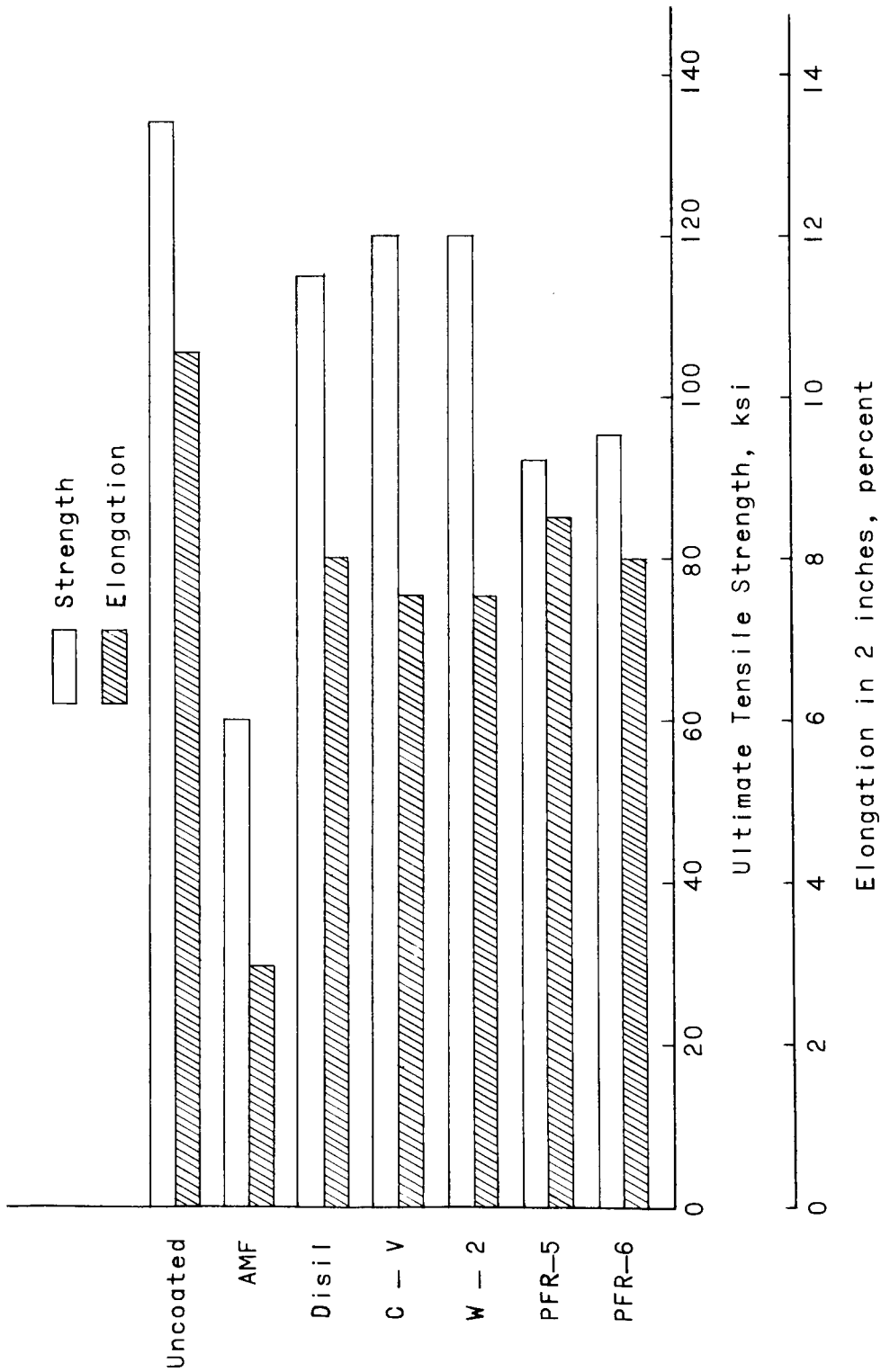
- 11 -



NASA

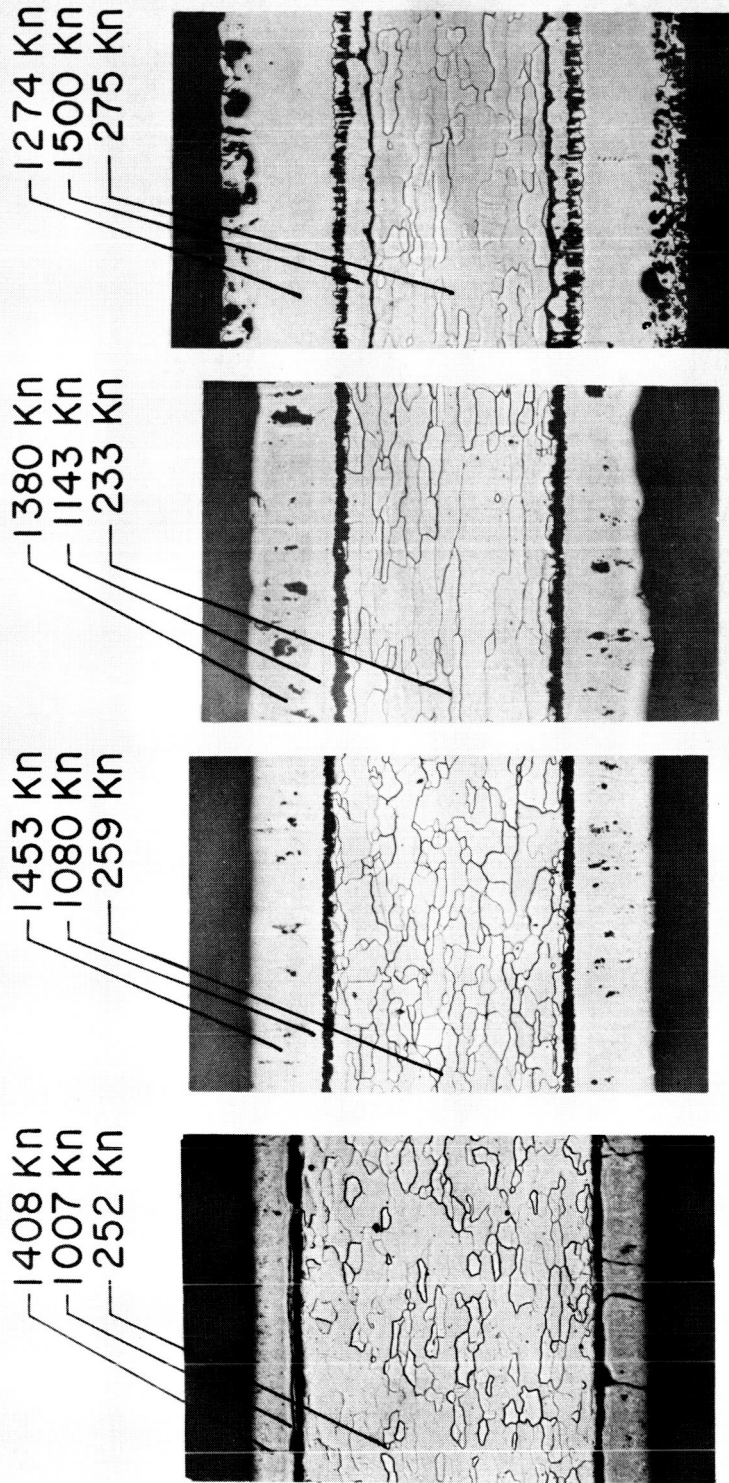
Figure 1.- Continuous and cyclic exposure coating life for various coatings on Mo-0.5 Ti molybdenum alloy sheet. (Reference 1.)

PRELIMINARY



NASA

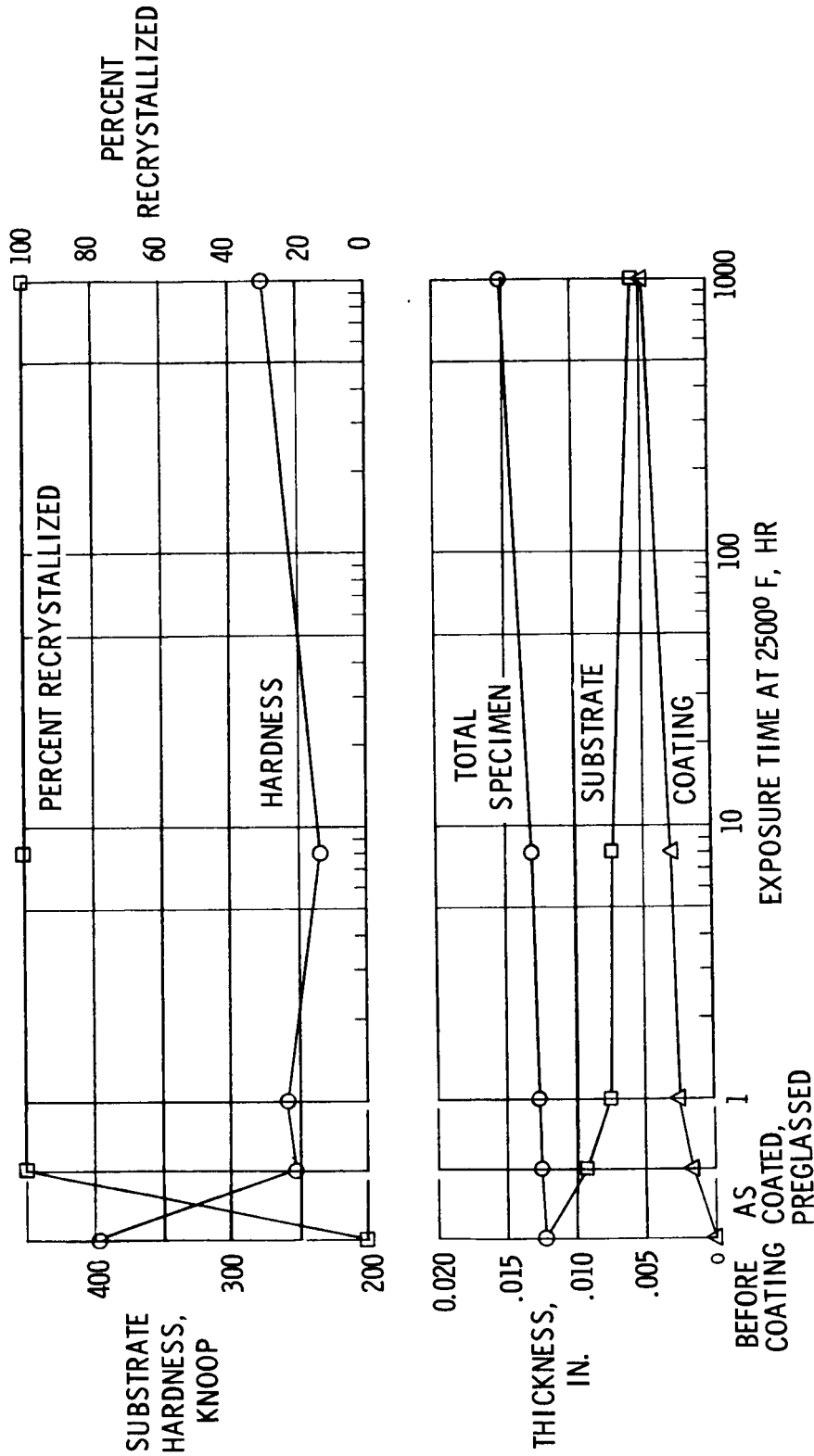
Figure 2.- Results of room temperature tensile tests of uncoated and coated Mo-0.5 Ti molybdenum alloy sheet specimens from reference 1. Strength is based on cross-sectional area before coating.



NASA

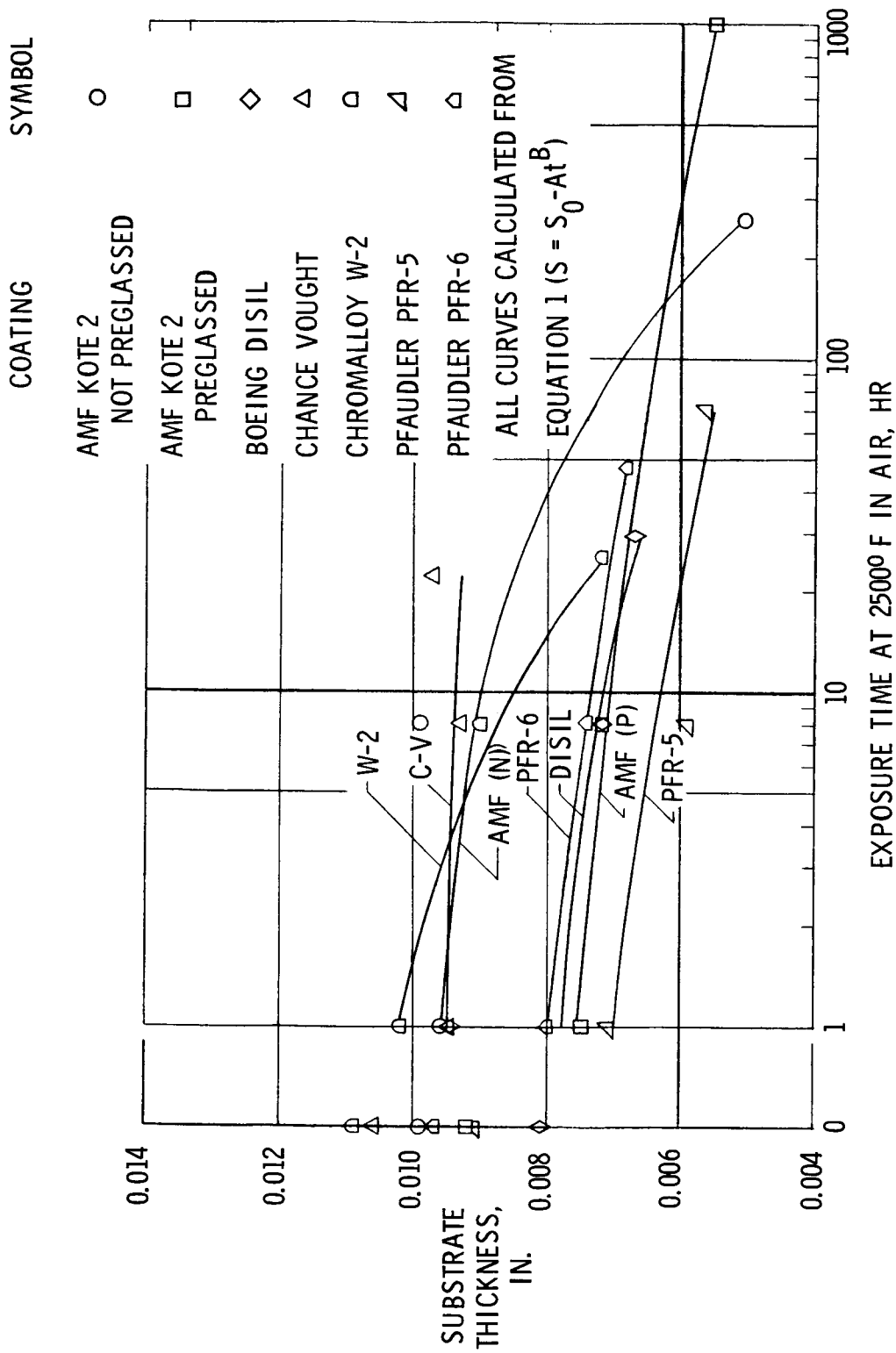
(a) As coated, preglassed. (b) After 1-hour exposure. (c) After 8-hour exposure. (d) After 1,000-hour exposure.

Figure 3.- Cross-sectional views of the AMF Kote 2 coating, preglassed on Mo-0.5 Ti after various 2500° F exposures in air, as noted. X 200.



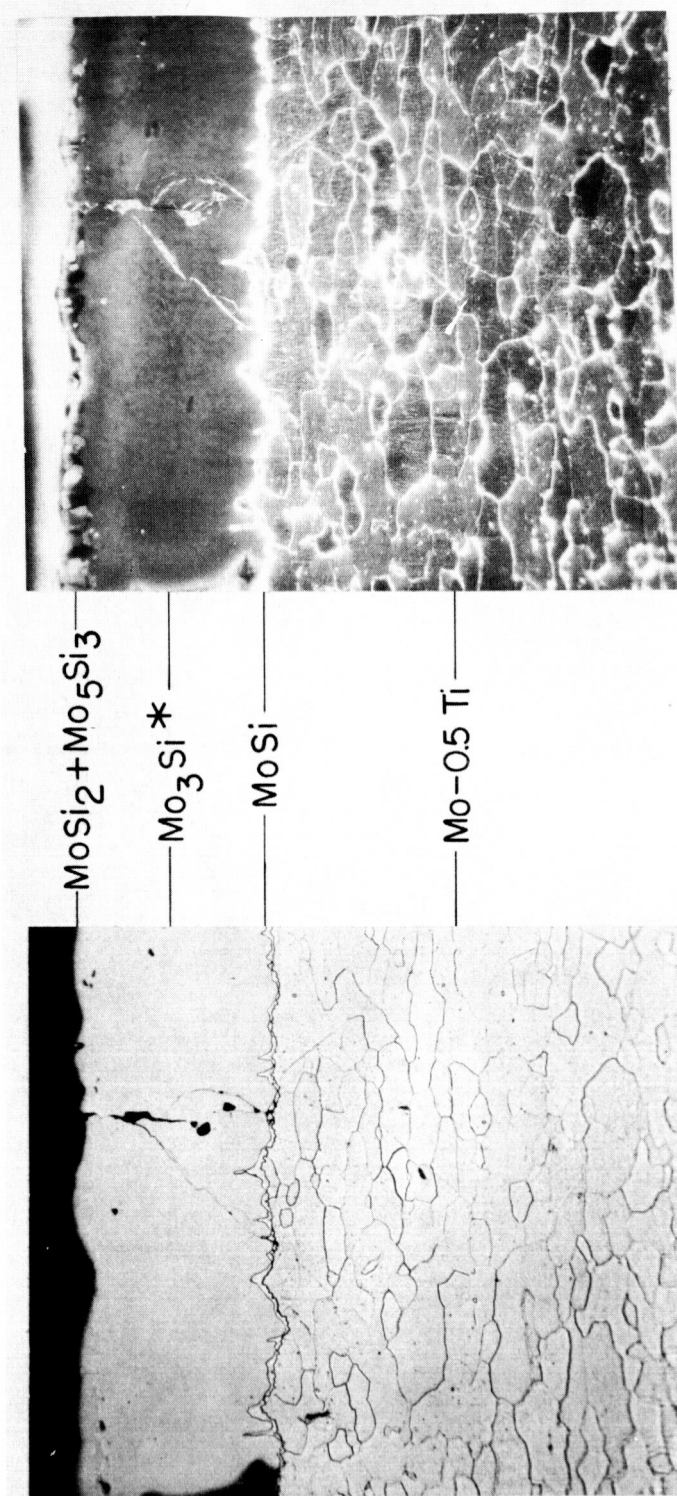
NASA

Figure 4.- Variation of substrate hardness, percent recrystallization, and total specimen, coating and substrate thickness with coating application and exposure time at 2500° F in air for the AMF Kote 2 coating, preglased, on Mo-0.5 Ti molybdenum alloy sheet.



NASA

Figure 5.- Comparison of experimentally determined substrate thickness decrease due to solid state diffusion (symbols) with empirical approximations calculated from equation (1) (curves) for the various coatings investigated on Mo-0.5 Ti molybdenum alloy sheet.



NASA

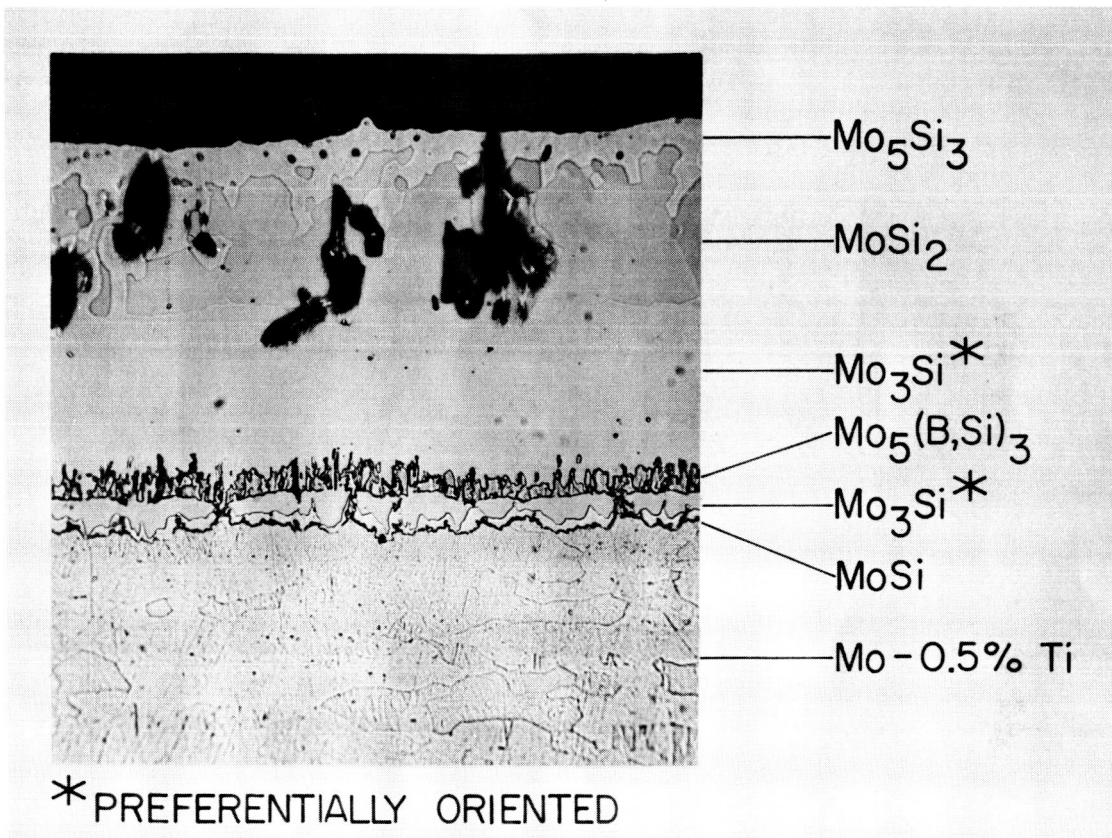
(b) Polarized light.

(a) Bright field illumination.

Figure 6.- Cross-sectional views of the Boeing Disil Coating on Mo-0.5 Ti after 20.7 hours at 2500° F in air. x 500.

PRELIMINARY

- 17 -



NASA

Figure 7.- Cross-sectional view of an AMF Kote 2 preglassed coated specimen after 120 hours at 2500° F in air. $\times 500$.